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Speciation of butyltin compounds in marine sediments by preconcentration on C_{60} and gas chromatography–mass spectrometry

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Abstract

A new method for the speciation of butyltin compounds by solid phase extraction and direct injection using gas chromatography–mass spectrometry (GC/MS) is described. The compounds were complexed with sodium diethyldithiocarbamate and retained on a C_{60} sorbent column. The neutral chelates of butyltin compounds were eluted with ethyl acetate containing $NaBPr_4$ as derivatising reagent. The main analytical figures of merit of the proposed method for 10 ml of sample are: linear range 0.2–35 ng/g expressed as Sn; limits of detection, 0.07, 0.09 and 0.10 ng/g as Sn for monobutyltin, dibutyltin and tributyltin, respectively. No interferences from metal ions such as Zn^{2+}, Fe^{3+}, Sb^{3+}, Pb^{2+}, Ni^{2+} and Mn^{2+} were observed in the determination of organotin compounds. The validation of method was performed out by the analysis of a standard reference sediment (CRM 462). The method was also applied to the determination of butyltin compounds in marine sediment samples.

Keywords: Speciation; Preconcentration; Butyltin compounds

1. Introduction

The determination of the chemical forms of elements is still an analytical challenge. Not only the oxidation state, but also the alkylation grade are of great interest, as they have different impact and behaviour in relation to toxicity, mobility and bioavailability. Generally, metal alkylation helps transport across the biological membrane and therefore accumulation in the food chain [1–3]. Thus, the major analytical target species include well-known organometallic environmental pollutants which have created environmental concern in the last few decades [4–7] such as butyl- and phenyltin, or alkyllead compounds. The great concern about these compounds is revealed by the number of reviews published on this topic in the last years [8–11]. The most toxic organotin species correspond to triorganotins, followed by di- and monoorganotin compounds. Organotin compounds have been extensively used as active ingredients of antifouling paints: their method of action consists of the release of toxic organotins in the surroundings of the boat to avoid the attachment of aquatic organism to the hull of the vessel. Thus, the major effect of organotin compounds contamination can be observed in harbours and marinas, where the ships are stationary, due to a build up in the concentration of toxicants. On the other hand, the short residence time of tributyltin (TBT) in water, with a half-life in the range of days to weeks [12,13], mainly due to its adsorption onto suspended particulated matter [14], together with the slow degradation of TBT in sediments (with a half-life from several months to almost 2 years [15,16]) lead to an increase of the persistence of this compound in the aquatic environment. Consequently, the determination of levels of TBT and its metabolites in marine sediments is essential in order to assess risks of environmental contamination.

The methods currently employed for the determination of organotin compounds in environmental matrices usually involve several steps; the extraction of the analytes from the sample is usually accomplished by liquid–liquid or solid–liquid conventional extraction procedures, although alternative techniques such as solid phase microextraction have been recently developed [17–19]. The current methods involve a separation technique (GC or LC) coupled with high sensitive and element specific detectors, such as mass spectrometry [19], atomic absorption spectrometry [20], atomic emission spectrometry [9,20], flame

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photometric [21], microwave inductively coupled plasma atomic emission spectrometry [22] and inductively coupled plasma mass spectrometry [23]. When using GC as separation technique, a derivatization step is needed in order to render the non-volatile organotin compounds into more volatile species. This derivatization can be accomplished by using hydride generation [24] or Grignard reagents [20,25,26], although hydride formation method is very prone to interferences from matrix and alkylation using Grignard reagents require a water-free medium the usually implies a tedious procedure with several handling steps. In the last years, alkylation using tetraethylborate [20,22] and more recently tetrapropylborate [27] have been successfully employed for the one-step aqueous derivatisation of organotin compounds in environmental samples.

In the present paper, a new method for the on-line preconcentration of butyltin compounds onto a C_{60} fullerene column and further determination of the analytes using gas chromatography–mass spectrometry (GC/MS) is described. From the discovery of fullerenes in 1985 [28], they have attracted the interest of the scientific community in several fields, including analytical chemistry, where they have been employed mainly for separation purposes, but also as sorbent materials [29]. They have proved to have excellent sorbent properties towards neutral chelates of metallic [30] as well as organometallic [31] species. When compared to traditional sorbents such as RP-C_{18}, C_{60} has proven to provide a higher selectivity towards π-donor species as well as wider working pH range [32]. In this case, a C_{60} fullerene column is used in a continuous flow system for the retention of butyltin compounds as neutral chelates that are later eluted and simultaneously derivatised using sodium tetrapropylborate to enable their injection into a GC/MS. The developed method has been validated using a certified reference material and applied to the analysis of superficial coast sediment samples collected in the south and south-east of Spain.

2. Experimental

2.1. Reagent and standard solutions

C_{60} fullerene (>99.4% purity) was obtained from Dynamic Enterprises Ltd. (Berkshire, UK). Stock solutions of *n*-butyltin trichloride (MBT) 95%, di-*n*-butyltin dichloride (DBT) 97% and tri-*n*-butyltin chloride (TBT) 96% were prepared by dissolving appropriate amounts of the respective salts (STREM Chemicals, Bischeim, France) in methanol. All butyltin standards were stored at 4 °C in the dark. Working standards solutions were prepared daily from the stock solutions by dilution with 0.2 M sodium acetate buffer solution (pH = 5.3). Solutions of 1.0×10^{-3} M sodium diethyldithiocarbamate (NaDDC) in water (Sigma–Aldrich, Madrid, Spain), 500 mg/l tetraethyllead (TeEL) in *n*-hexane (Sigma–Aldrich) and 1.2 M sodium tetra-*n*-propylborate 98% in ethanol (Galab, Geesthacht, Germany) were also prepared. Aqueous solutions of other metals (Zn^{2+}, Fe^{3+}, Sb^{3+}, Pb^{2+}, Ni^{2+}, Mn^{2+}, Co^{2+}, Cu^{2+}, 1 g/l) were prepared for interference studies. Organic solvents and other chemical reagents were reagent grade purity at least and were purchased from Scharlau (Barcelona, Spain). Certified reference material was obtained from the Community Bureau of Reference (BCR, Commission of the European Communities, Brussels, Belgium): CRM 462 coastal sediment.

2.2. Apparatus

Experiments were carried out by using a Fisons gas chromatograph 8000 interfaced to a Fisons MD 800 mass spectrometer and controlled by a computer running MASSLAB software (Thermo-Quest, Madrid, Spain). GC separations were run on a fused silica capillary column (30 m × 0.25 mm i.d.) coated with 5% phenylmethyl-polysiloxane (film thickness 0.25 μm) (Supelco, Madrid, Spain). The injection port, transfer line and detector temperatures were maintained at 250, 250 and 200 °C, respectively, throughout the experiments. The temperature of the chromatographic oven was programmed as follows: held at 50 °C for 1 min, raised up to 250 °C at 30 °C/min and held again for 1.5 min. In all the analyses, a volume of 1 μl of sample was injected in split mode (1:25 ratio). Helium (6.0 grade, Air liquide, Seville, Spain), regulated at a flow rate 1 ml/min by a digital pressure and flow controller was used as carrier gas. The mass spectrometer was used in the electron impact ionization mode (70 eV), over the scan range *m*/*z* 70–500. Peak area was chosen as the analytical signal for quantification purposes. The following *m*/*z* values were selected for each derivative compound (quantification mass in italic): MBT^{3+} 121, 165, 207, *263*; DBT^{2+} 121, 179, 221, *277*; TBT^{+} 121, 179, 221, *277*, 291.

The flow injection (FI) manifold consisted of a Gilson Minipuls-2 peristaltic pump (Villiers-le-Bel, France) furnished with poly(vinylchloride) tubing, two Rheodyne 5041 injection valves (Cotati, CA, USA), PTFE tubing of 0.5 mm i.d. and a laboratory-made sorption column (C_{60} fullerene, 80 mg) made out of PTFE capillary of 3 mm i.d. and sealed at both ends with small glass-wool plugs to prevent losses of sorbent material.

2.3. Samples preparation

2.3.1. Spiking procedure

For recovery studies, uncontaminated sediment samples were treated as follows: 10 g of sediment samples were spiked with a mixture of MBT, DBT and TBT at low (0.3 ng/g), medium (10 ng/g) and high (30 ng/g) concentration contained in 1 ml of methanol. Then the samples were shaken magnetically for 1 h and the solvent was evaporated at room temperature. After that, the samples were frozen at −20 °C until their analysis. A blank sample was prepared following the same procedure.

2.3.2. Extraction procedure

Spiked samples as well as real marine sediment samples collected at different locations in the south and south-east of Spain were extracted according to the next procedure: 1 g of dried sediment sample was weighed in a beaker and treated with a mixture of 1 ml glacial acetic acid, 3 ml of methanol and 6 ml acetate buffer 0.2 M, being the pH adjusted to pH 5.3. The sample was then sonicated for 45 min in an ultrasonic bath and centrifuged at 3000 rpm for 15 min. The solid pellet was discarded and the supernatant was taken to a final volume of 10 ml. A blank sample was prepared in parallel. The reliability of the SPE-GC/MS method was evaluated through the analysis of a reference material (CRM 462).

2.4. Analytical procedure

The FI system employed for the continuous preconcentration/elution is shown in Fig. 1. The resulting extract (10 ml) from the leaching procedure at pH 5.3 containing butyltin species was aspirated (flow rate 2.8 ml/min) and mixed with a 1.0×10^{-3} M NaDDC stream (flow rate 0.5 ml/min). Diethyldithiocarbamate complexes were formed in the reaction coil (150 cm) and then sorbed onto the C_{60} fullerene column. After the preconcentration step, an air stream (flow rate 5.0 ml/min) was used to remove any residual water from the system and then as carrier of the eluent/derivatising reagent (24×10^{-3} M $NaBPr_4$ in ethyl acetate containing 0.5 mg/l TeEL as internal standard). The extract (200 μl) was collected in an eppendorf vial where the propylation reaction was completed within 1.3 min. Aliquots of 1 μl of the ethyl acetate phase were manually injected into the GC/MS. The C_{60} column was flushed with 200 μl *n*-hexane after each working day.

3. Results and discussion

3.1. Optimisation of the method

As stated in previous sections, the preconcentration of butyltin compounds is based on the formation of neutral chelates that are later adsorbed onto the surface of the C_{60} fullerene sorbent column. The elution step comprises also a derivatisation reaction with $NaBPr_4$ in order to render the ionic alkyltin compounds into volatile species suitable for their determination by GC/MS. The flow system depicted in Fig. 1 was the result of an exhaustive study on the most relevant variables affecting the performance of the method, including flow as well as chemical variables. Unless stated otherwise, a volume of 10 ml a standard solution containing a mixture of MBT, DBT and TBT (3 ng/ml each) was used throughout the optimisation experiments.

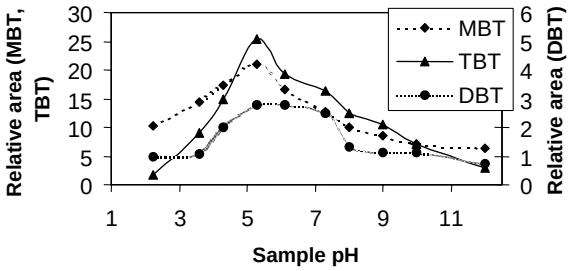

Fig. 2. Effect of sample pH on the derivatisation/retention of butyltin species on C_{60} fullerene. Sample containing 3 ng/ml of each butyltin compound in a volume of 10 ml.

3.1.1. Chemical variables

The initial pH the sample is a decisive factor, since the retention of the analytes on the sorbent column depends on the formation of a neutral chelate, and this is only possible when the complexation reaction is favoured versus the hydrolysis of the butyltin compounds leading to Sn^{4+} in acidic medium or to $Sn(OH)_4$ in basic conditions. In order to study the pH dependence of the system, 10 ml standard solutions of MBT, DBT and TBT (3 ng/ml each) were adjusted to pH values ranging between 2 and 12 using diluted sodium hydroxide and diluted hydrochloride acid. The result is shown in Fig. 2. As can be seen TBT and MBT present a narrow optimum pH range (5.1–5.5), while this range is wider for DBT. Since TBT is the butyltin specie showing a higher

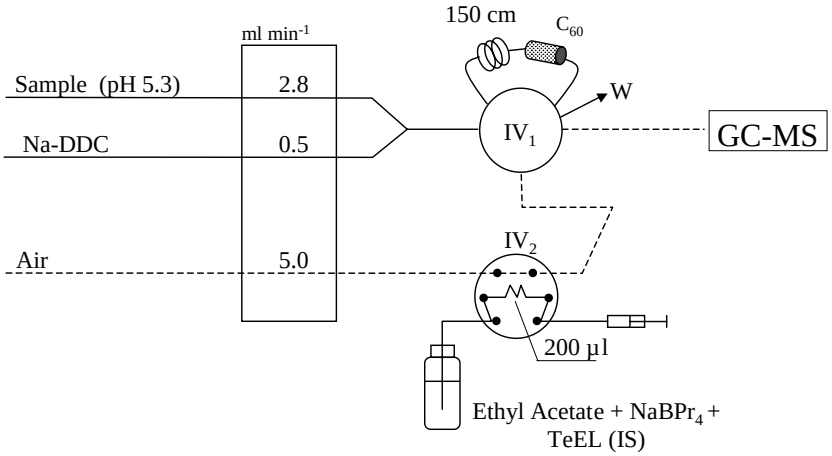

Fig. 1. Flow injection manifold for the speciation of butyltin compounds: IV, injection valve; W, waste; GC/MS, gas chromatograph–mass spectrometer.

toxicity, the method is specially optimised to enhance its determination; for that reason, the pH of the sample was adjusted to 5.3 for further experiments.

The next step was the selection of the chelating reagent. It is well known that Sn^{4+} forms stable chelates with NaDDC and APDC, so both reagents were studied in a concentration of 1.0×10^{-3} M and their performance compared. The method provided very similar results in both cases, although slightly more sensitive for NaDDC, so this reagent was selected. The retention was found not to be strongly dependent on the NaDDC concentration in the range from 0.5×10^{-3} to 3.5×10^{-3} M. A concentration value of 1.0×10^{-3} M was selected in order to ensure a proper excess of chelating reagent to complex not only the analytes but also other cations that could be present and act as possible interferences.

The selection of the eluent is of special relevance in this case since it is not only the elution, but also the derivatisation medium. Organic solvents of different polarity were tested containing the same amount of $NaBPr_4$ (derivatising agent), such as methanol, ethanol, petroleum ether, ethyl acetate, chloroform and *n*-hexane. The best results were obtained when using ethyl acetate as eluent. Concerning the derivatising reagent, $NaBPr_4$ was selected according to the satisfactory results described in literature for organometallic compounds. The concentration of it was studied between 9×10^{-3} and 24×10^{-3} M. The best performance was observed with higher concentrations; a solution of $NaBPr_4$ 24×10^{-3} M in ethyl acetate was selected as the eluent/derivatising reagent. In these conditions, the derivatisation reaction proceeded in a very short time, so that a time of 1.3 min was enough to ensure the complete propylation of the butyltin compounds.

3.1.2. Flow variables

The different flow variables affecting the system were also optimised (see Fig. 1). The sample flow rate had not a significant influence within the studied range (from 0.5 to 3.5 ml/min), so a value of 2.8 ml/min was selected in order to shorten the analysis time. The chelating agent flow rate was studied up to 1 ml/min, the signal increasing with the flow rate from 0.2 to 0.4 and remaining constant beyond that value. Thus, a flow rate of 0.5 ml/min was used in further experiments. The carrier (air) flow rate is also especially relevant in this case since its function is not only to lead the eluent through the sorbent column but also to remove the remaining water from the system tubing. A wide range of flow rates was studied (2.0–5.8 ml/min), and the performance was found not to improve beyond 5.0 ml/min, so this flow rate was selected.

The length of the reaction coil was also optimised; the range between 45 and 250 cm was studied, and the signal remained constant above 150 cm, which was selected for all subsequent experiments. The elution volume was varied between 100 and 350 μl. A volume of 200 μl was found to be the first one showing no carry over in subsequent elutions; higher volumes increased dilution, reducing thus the sensitivity especially for DBT and TBT.

Under the selected conditions, the breakthrough volume was also studied. The maximum volume of sample that can be passed through the sorbent column (80 mg C_{60} fullerene) without analyte losses was found to be 25 ml.

Table 1
Analytical figures of merit of the determination of butyltin compounds

	MBT	DBT	TBT
Retention time (min)	6.4	6.8	7.2
m/*z* selected[a]	263	277	277
Detection limit (pg/μl as Sn)[b]	0.007	0.009	0.010
Linear range (ng/ml as Sn)[b]	0.02–3.0	0.03–3.5	0.03–3.5
Correlation coefficient (r^2)	0.999	0.996	0.997
Precision (R.S.D., %)	7	6	7

[a] Internal standardization used (TeEL, $t_r = 5.01$ min, $m/z = 237$).
[b] Extract volume, 10 ml.

Table 2
Tolerated concentrations of foreign cations in the determination of 3 ng/ml of butyltin compounds (expressed as Sn)

Cation	MBT	DBT	TBT
Fe^{3+}	50–1000[a]	200–1000[a]	200–1000[a]
Sb^{3+}	200	200	200
Pb^{2+}	1000	1000	1000
Cu^{2+}	50	1000	1000
Mn^{2+}	1000	1000	1000
Co^{2+}	50	50	1000
Ni^{2+}	1000	1000	1000
Zn^{2+}	1000	1000	1000

[a] Tolerated ratio in 0.2 M buffer acetate pH 5.3.

3.2. Analytical features of the method

Using the described optimised system, calibration graphs were run for standard mixtures containing the three analytes (sample volume 10 ml). The results are shown in Table 1. As can be seen, the linear range is very similar for all the analytes, ranging from 0.02 to 3.5 ng/ml (corresponding to 0.2–35 ng/g of sediment). The detection limits, calculated as the concentration leading to a signal corresponding to

Table 3
Determination of butyltin compounds in marine sediment samples

Sample	Concentration found (ng/g)		
	MBT	DBT	TBT
CRM 462[a]		68 ± 12	54 ± 15
CRM 462[b]	110 ± 22	62 ± 13	48 ± 10
CRM 462[c]	112 ± 21	79 ± 11	42 ± 17
1	1.15 ± 0.12	0.53 ± 0.06	2.1 ± 0.2
2	0.24 ± 0.03	0.42 ± 0.05	0.45 ± 0.06
3	0.27 ± 0.03	0.38 ± 0.05	0.35 ± 0.04

[a] Certified value as butyltin compounds.
[b] Values obtained by the proposed method.
[c] Data from [19].

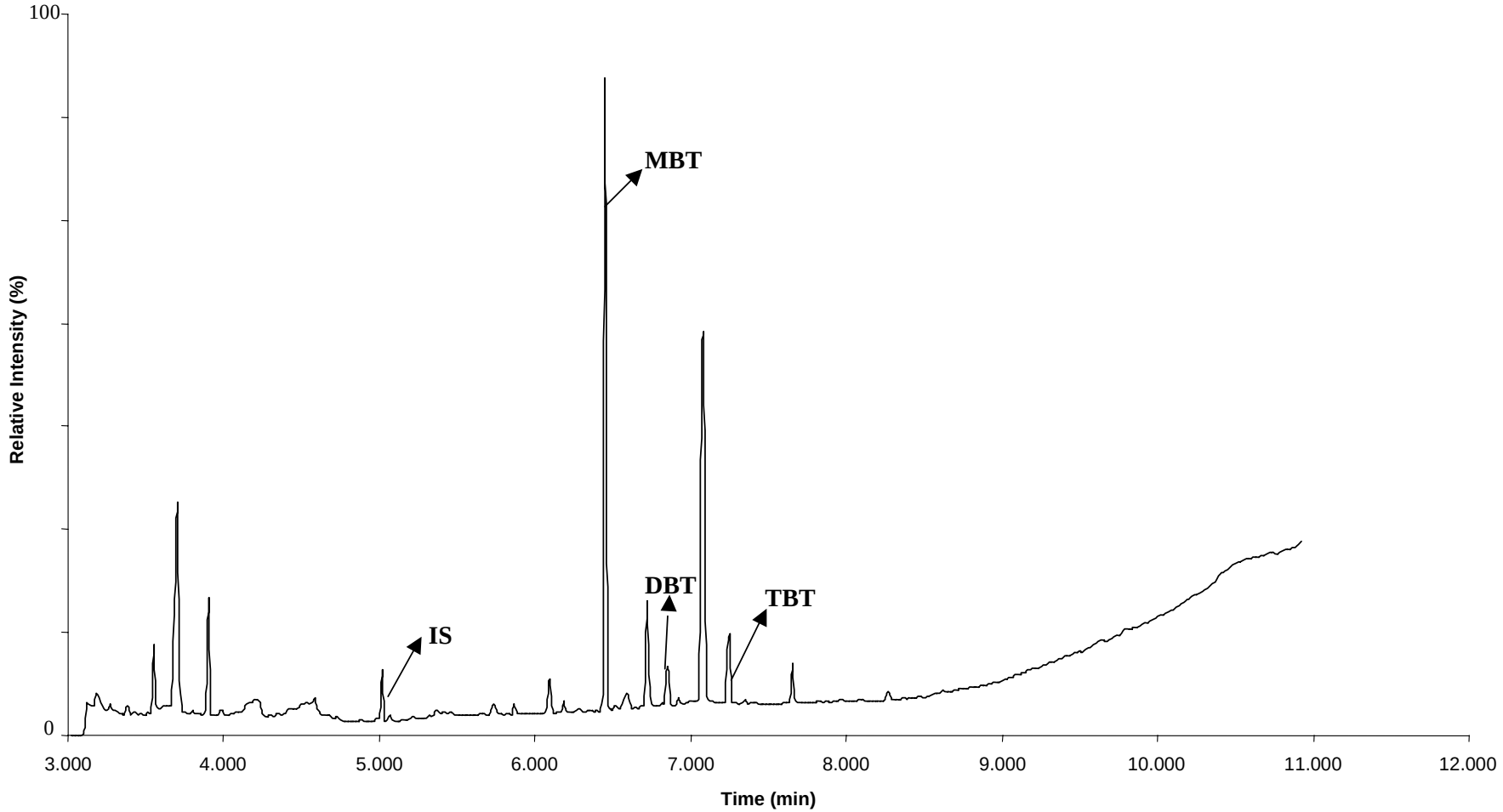

Fig. 3. Chromatogram of butyltin compounds extracted from a superficial coast sediment sample (no. 1 in Table 3) collected in the south of Spain.

three times the standard deviation of the noise, ranged from 7 to 10 ng/l (0.07–0.10 ng/g), suitable for the usual concentrations found in 10 ml extracts of sediment samples. The precision of the method, expressed as relative standard deviation (evaluated by analysing 11 standards solutions containing 1 ng/ml of each analyte) is also listed in Table 1.

3.3. Interferences study

Due to the nature of the basis of the method, the performance can be significantly affected in the case that the formation/retention of the neutral chelates is precluded. This is true when metallic ions are present that can also form chelates with NaDDC, competing then with the analytes for the chelating reagent or for the active sites on the surface of the fullerene sorbent column. The first mechanism is easily prevented by employing an excess of NaDDC as stated in the optimisation section. In order to evaluate the influence of the presence of other metallic ions, solutions of the analytes (MBT, DBT, TBT, 3 ng/ml) together with Fe^{3+}, Sb^{3+}, Pb^{2+}, Mn^{2+}, Cu^{2+}, Ni^{2+}, Co^{2+} or Zn^{2+} (up to 3 μg/ml) were analysed using the described flow system. The maximum tolerated ratio of each foreign cation relative to the content of tin in the organometallic compound is shown in Table 2. As can be seen, the method is selective versus most of the metals, being only Fe^{3+}, Cu^{2+} and Co^{2+} the potential interferences but in concentrations above 50-fold times that of tin compounds. Several additional reagents were employed in order to minimise the effect of these metals. The interference of Fe can be eliminated by preparing samples in acetate buffer 0.2 M at pH 5.3, since Fe forms a very stable negatively complex that is not retained on the fullerene column. In these conditions, the tolerated ratio is increased up to 1000. However, the interferences of Cu^{2+} and Co^{2+} could not be reduced even after treatment with a general complexing reagent such as ethylenediaminetetraacetic acid (EDTA) 0.1 M. Nevertheless, taking into account the small concentrations of these metals in real samples the method can still be applied without special concern.

3.4. Validation of the method

The reliability of the method was checked by two different approaches: on the one hand, recovery studies were performed on coast sediments previously analysed to confirm the absence of the analytes. Butyltin compounds were added at low (0.3 ng/g), medium (10 ng/g) and high (30 ng/g) concentrations following the procedure described in detail in Section 2.3.2. Recoveries between 80 and 90% for MBT and 85 and 95% for DBT and TBT were obtained.

On the other hand, a certified reference material (CRM 462) for the values of TBT and DBT in coast sediment was also analysed by the proposed method. For this purpose, 1 g of sample was dried in an oven at 102 ± 2 °C for 3–4 h (according to manufacturer's recommendations). The concentrations found are shown in Table 3. As can be seen, they are in concordance with the certified values as well as with other methods described in the literature and employed for the analysis of the same reference material. In conclusion, the method can be considered as validated according to recognised procedures.

3.5. Application to environmental samples

The proposed method has been applied to the analysis of superficial coast sediment samples (mainly consisting of sand and with a TOC lower than 0.5%) collected in different locations of Spain. The concentrations (ng/g dry weight, ±S.D., $n = 5$) found can be seen in Table 3. Sediment 1 was sampled in the neighbourhood of a fishing harbour (Málaga, Spain), while samples 2 (Almería, Spain) and 3 (Valencia, Spain) were collected in clean shores. As expected, the butyltin concentrations are higher in the sample collected close to the harbour, due to the contamination of the antifouling paintings employed for the protection of the fishing boats. A typical chromatogram showing the three analytes is shown in Fig. 3.

4. Conclusions

A new, simple, and automated flow system for the speciation of butyltin compounds in environmental samples by GC/MS has been developed. The proposed system allows for the determination of MBT, DBT and TBT in concentrations in the ng/g range thanks to the preconcentration of the analytes as neutral chelates on a fullerene C_{60} sorbent column. The high adsorption capacity of this sorbent enables its use even in presence of other metals, being Cu^{2+} and Co^{2+} in high concentrations the only interferences. The reliability of the method has been validated by performing a recovery study on real samples and furthermore by the analysis of a certified reference material, proving its capability for environmental samples analysis.

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